Preferential Solvation of Silver(I) Bromate in Methanol-Dimethylsulfoxide Mixtures

S. Janardhanan and C. Kalidas
Department of Chemistry, Indian Institute of Technology, Madras-600 036, India

Z. Naturforsch. 39a, 600–602 (1984); received March 13, 1984

The solubility of silver bromate, the Gibbs transfer energy of Ag⁺ and BrO₃⁻ and the solvent transport number in methanol-dimethyl sulfoxide mixtures are reported. The solubility of silver bromate increases with addition of DMSO. The Gibbs energy of transfer of the silver ion (based on the ferrocene reference method) decreases, while that of the bromate ion becomes slightly negative with the addition of DMSO. The solvent transport number J passes through a maximum (J = 1.0 at X_DMSO = 0.65). From these results, it is concluded that the silver ion is preferentially solvated by DMSO whereas the bromate ion shows no preferential solvation.

Introduction

Preferential solvation of ions in mixed solvents profoundly affects the solubilities, rates of chemical reactions, phase separation in binary mixtures and electrode potentials [1]. It finds application in the electrorefining and electrowinning of metals [2, 3]. Further, the sign and magnitude of the solvent transport number provide valuable information on the composition of the solvation shells of ions in mixed solvents [4].

The selective solvation behaviour of some silver salts in water-DMSO mixtures, which possess strong solvent-solvent interaction, has received considerable interest in recent years [5, 6]. The present paper deals with the selective solvation of silver bromate in methanol-DMSO mixtures, whose solvent-solvent interaction differs markedly [7] from that of water-DMSO mixtures.

Materials and Methods

DMSO and methanol were purified as described in [8]. The preparation of silver bromate has been reported in [6]. The solubility measurements in the solvent mixtures were carried potentiometrically as described in [6]. The silver electrodes required for the emf measurements were prepared by electrolytically coating silver onto platinum wires sealed in glass tubes according to the method of Carmody [9].

The solvent transport number J in methanol-DMSO mixtures was determined by setting up a concentration cell as suggested by Wagner [10], in which the two half cells are saturated with silver bromate and the mole fraction difference of DMSO was then calculated from

Reprint requests to Prof. C. Kalidas, Department of Chemistry, Indian Institute of Technology, Madras-600 036 India.

Results and Discussion

The solubility, S, of silver bromate and the solubility product, K_{sp}, of the salt calculated from

Further details have been described in [6].

On 01.01.2015 it is planned to change the License Conditions (the removal of the Creative Commons License condition "no derivative works"). This is to allow reuse in the area of future scientific usage.

Dieses Werk wurde im Jahr 2013 vom Verlag Zeitschrift für Naturforschung in Zusammenarbeit mit der Max Planck Gesellschaft zur Förderung der Wissenschaften e.V. digitalisiert und unter folgender Lizenz veröffentlicht: Creative Commons Namensnennung-Keine Bearbeitung 3.0 Deutschland Lizenz.

Zum 01.01.2015 ist eine Anpassung der Lizenzbedingungen (Entfall der Creative Commons Lizenzbedingung „Keine Bearbeitung“) beabsichtigt, um eine Nachnutzung auch im Rahmen zukünftiger wissenschaftlicher Nutzungsformen zu ermöglichen.

This work has been digitalized and published in 2013 by Verlag Zeitschrift für Naturforschung in cooperation with the Max Planck Society for the Advancement of Science under a Creative Commons Attribution-NoDerivs 3.0 Germany License.
Table 1. Dielectric constant $\epsilon$ of methanol-DMSO mixtures, solubilities $S$ and transfer energies $^a$ of the salt and the silver and bromate ions at 30°C.

<table>
<thead>
<tr>
<th>Mole fraction of DMSO</th>
<th>$\epsilon$</th>
<th>$S \times 10^2$ mol kg$^{-1}$</th>
<th>$^{AG^0}_{(AgBrO_3)}$ kcal mol$^{-1}$</th>
<th>$^{AG^0}_{(Ag^+)}$ kcal mol$^{-1}$</th>
<th>$^{AG^0}_{(BrO_3^-)}$ kcal mol$^{-1}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.0</td>
<td>31.80</td>
<td>0.005</td>
<td>0.0</td>
<td>0.0</td>
<td>0.0</td>
</tr>
<tr>
<td>0.1</td>
<td>33.75</td>
<td>0.024</td>
<td>-1.86</td>
<td>-1.15</td>
<td>-0.71</td>
</tr>
<tr>
<td>0.2</td>
<td>38.80</td>
<td>0.079</td>
<td>-3.26</td>
<td>-2.42</td>
<td>-0.84</td>
</tr>
<tr>
<td>0.3</td>
<td>41.60</td>
<td>0.186</td>
<td>-4.26</td>
<td>-3.50</td>
<td>-0.76</td>
</tr>
<tr>
<td>0.4</td>
<td>44.00</td>
<td>0.362</td>
<td>-5.03</td>
<td>-4.50</td>
<td>-0.53</td>
</tr>
<tr>
<td>0.5</td>
<td>45.20</td>
<td>0.640</td>
<td>-5.68</td>
<td>-5.25</td>
<td>-0.43</td>
</tr>
<tr>
<td>0.6</td>
<td>46.01</td>
<td>1.00</td>
<td>-6.18</td>
<td>-5.88</td>
<td>-0.30</td>
</tr>
<tr>
<td>0.7</td>
<td>46.45</td>
<td>1.54</td>
<td>-6.66</td>
<td>-6.35</td>
<td>-0.31</td>
</tr>
<tr>
<td>0.8</td>
<td>46.60</td>
<td>2.20</td>
<td>-7.05</td>
<td>-6.69</td>
<td>-0.36</td>
</tr>
<tr>
<td>0.9</td>
<td>46.45</td>
<td>3.03</td>
<td>-7.40</td>
<td>-7.00</td>
<td>-0.40</td>
</tr>
<tr>
<td>1.0</td>
<td>46.00</td>
<td>3.79</td>
<td>-7.64</td>
<td>-7.26</td>
<td>-0.38</td>
</tr>
</tbody>
</table>

$^a$ $^{AG^0}$ values accurate to ± 0.05 kcal/mol.

and the transfer energy of the anion in these mixtures calculated from

$$^{AG^0}_{(AgBrO_3)} = ^{AG^0}_{(Ag^+)} + ^{AG^0}_{(BrO_3^-)}$$

are also given in Table 1.

The Gibbs energy of transfer of AgBrO$_3$ (Table 1) continuously decreases from methanol to DMSO. The transfer energy of the bromate ion in slightly negative less than 0.5 kcal/mol beyond $X_{DMSO} = 0.4$) at all solvent compositions and thus appears to be not preferentially solvated by methanol or DMSO. The Gibbs transfer energy of the silver ion, however, continuously decreases with the addition of DMSO indicating that it is selectively solvated by DMSO in these mixtures.

**Solvent Transport Number Measurements**

The EMF data of the Wagner cell [10] in these mixtures and the solvent transport numbers calculated from these data using the relation

$$E = -\frac{RT}{F} \left( \frac{X'_S - X'_S}{X_S(1-X_S)} \right) \Delta \left( 1 + \frac{\partial \ln f_S}{\partial \ln x_S} \right)$$

where $X'_S = \frac{1}{2}(X'_S + X'_S)$ ($S$ = DMSO in the present case), are given in Table 2. The activity coefficient term in (4) accounts for the non-ideal behaviour of the solvent mixtures, and $X'_S - X'_S = 0.1$ was maintained throughout. The $\Delta$ values are positive throughout with a maximum value of 1.0 around $X_{DMSO} = 0.65$, indicating that a net increase of 1.0 mole of DMSO per Faraday (relative to the mean molar velocity of the solvent mixture as reference) occurs in the cathode compartment when solutions of the salt are electrolysed at the given composition of the solvent mixture. The solvent transport number of DMSO is related to the partial solvation numbers of cation and anion and the ionic transfer numbers [11]:

$$\Delta = \Delta_+ - \Delta_-$$

$$\Delta_+ = (X_M n_D^+ - X_D n_M^+) t_+$$

$$\Delta_- = (X_M n_D^- - X_D n_M^-) t_-$$

where the $X$'s refer to the mole fractions of the two solvent components and the $n$'s refer to the partial solvation numbers of $Ag^+$ and anion by the solvents indicated by the subscripts. $\Delta_+$ and $\Delta_-$ are the solvent transport numbers due to the cation and anion. In the present case, the anionic contribution to the solvent transport, i.e. $\Delta_-$, appears to be negligible in view of the fact that $^{AG^0}_{(BrO_3^-)} \approx 0$, and thus the considerable positive $\Delta$ values observed in this case are entirely due to the transport of DMSO towards the cathode by the silver ion.